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Chemical kinetic modeling of component mixtures relevant to gasoline

M. Mehl[1], H. J. Curran[2], W. J. Pitz[1], S. Dooley[2], C. K. Westbrook[1]

1. Lawrence Livermore National Laboratory - USA
2. NUI Galway - IRELAND

1. Introduction

Detailed kinetic models of pyrolysis and combustion of hydrocarbon fuels are nowadays widely used in the design of internal combustion engines and these models are effectively applied to help meet the increasingly stringent environmental and energetic standards. In previous studies by the combustion community, such models not only contributed to the understanding of pure component combustion, but also provided a deeper insight into the combustion behavior of complex mixtures. One of the major challenges in this field is now the definition and the development of appropriate surrogate models able to mimic the actual features of real fuels.

Real fuels are complex mixtures of thousands of hydrocarbon compounds including linear and branched paraffins, naphthenes, olefins and aromatics. Their behavior can be effectively reproduced by simpler fuel surrogates containing a limited number of components. Aside the most commonly used surrogates containing iso-octane and n-heptane only, the so called Primary Reference Fuels (PRF), new mixtures have recently been suggested to extend the reference components in surrogate mixtures to also include alkenes and aromatics. It is generally agreed that, including representative species for all the main classes of hydrocarbons which can be found in real fuels, it is possible to reproduce very effectively in a wide range of operating conditions not just the auto-ignition propensity of gasoline or Diesel fuels, but also their physical properties and their combustion residuals [1].

In this work, the combustion behavior of several components relevant to gasoline surrogate formulation is computationally examined. The attention is focused on the autoignition of iso-octane, hexene and their mixtures.

Some important issues relevant to the experimental and modeling investigation of such fuels are discussed with the help of rapid compression machine data and calculations. Following the model validation, the behavior of mixtures is discussed on the basis of computational results.

2. The kinetic mechanism

In the last year an extensive review based on recent experimental data involved the detailed kinetic mechanisms by LLNL for n-heptane, iso-octane and toluene. One of the main goals is the achievement of a comprehensive and reliable database of mechanisms that can be merged together to simulate the behavior of complex fuel surrogates. The mechanism discussed in this paper represents a step in this process.

A recent improvement in the n-heptane mechanisms was the introduction of the low temperature reaction pathways for some unsaturated hydrocarbons (e.g. 1-hexene …). The hexenes submechanism is right now subjected to validation and will be the reference to further extensions of alkene models.

The last revision of iso-octane mechanism involved a better definition of the decomposition reactions of the iso-octyl radicals and of the thermal properties of the neo-pentyl radical. These changes reduced significantly the reactivity of iso-octane in the intermediate temperature region.

The n-heptane and iso-octane mechanisms were merged into a detailed kinetic model for the simulation of surrogates including about 1250 species and 5300 reactions. The general structure of the resulting mechanism is based on a C_1-C_4 core and two main blocks: the first one includes all the main reaction pathways for the saturated and non saturated linear hydrocarbons up to C_7, the second one contains the same classes of reactions for branched hydrocarbons from C_5 to C_8. The interaction among the oxidation pathways of the different components of the mixture here analyzed are accounted for by the reactions of smaller radicals contained in the core mechanism and by a specific block of reactions involving the peroxyl radicals of the different fuels.

The thermodynamic properties of all the species included in the mechanism were evaluated using the THERM program developed by Ritter and Bozzelli, implementing Benson's group additivity method [2]. A detailed description of each submechanism can be found in [3-5].

3. Mechanism validation

The kinetic model here discussed has been validated in a wide range of operating conditions and of reactor designs. Since the main purpose of such kind of model concerns engine modeling issues, in the following paragraph the attention will be focused on the low temperature (650-1100K) high pressure (>10bar) autoignition regimes.

Rapid Compression Machine (RCM) and Shock Tube experiments are generally used to investigate this field of operating conditions. In particular, RCM are often assumed to reproduce the typical conditions taking place in a reciprocating engine; therefore RCM data are often used as a benchmark for kinetic models aimed to the simulation of engine combustion. Practically they are commonly simulated as totally or nearly adiabatic reactors where reactions start at the top dead center (TDC) conditions and the following pressure and temperature evolution is controlled by a constant volume combustion process. This assumption is reasonably correct whenever both the compression stroke and the autoignition process take place in short times; on the contrary, when long induction times or slow piston motion are involved, a better characterization of the reaction chamber volume history is fundamental. In practical devices when the TDC is reached, unreacted mixture is stratified into an adiabatic core and a colder boundary layer which exchange heat with the combustion chamber walls. While the core gasses have very limited heat losses, the cooling of the boundary layer causes the pressure (and consequently the temperature) inside the combustion chamber to drop depending on the chamber insulation and on the heat capacity of the gasses.

Other difficulties can be due to temperature inhomogeneities and to hot spots which result in flame propagation phenomena overlapping to the volumetric autoignition.

In this work the autoignition behavior of pure iso-octane, 1-hexene and their mixtures is analyzed.

Although the oxidation behavior of linear paraffins is generally well known, alkene reactivity has been poorly investigated. As far as branched hydrocarbons are concerned, some unclear aspects are extant. The long ignition delays characterizing this class of fuels, primarily iso-octane itself, make more difficult to obtain reliable direct measurements without incurring in the undesired non ideal behavior of the experimental device previously described. Recent measurements highlighted that a satisfactory convergence among the model and the different experimental information is not achieved yet.

For this reasons a recent work by Sung and coworkers was aimed to a careful characterization

of the compression stroke and heat release process affecting their RCM experimental results [6]. In the following paragraphs the computational results obtained with the oxidation mechanism by LLNL are compared with this recent set of experimental data and the earlier Lille RCM data [7]. Along with these experiments, some more sets of measurements obtained at different facilities but similar conditions are shown (Leeds [8], Michigan [9]), including the very recent one collected at NUI, Galway.

3.1. *Iso-octane comparisons*

Figure 1 shows the ignition delay times measured for iso-octane stoichiometric mixtures in different RCM facilities at similar conditions. Pressure and temperature ranges respectively span between 12-16 atm and 650K-1000K, and stoichiometric conditions are considered. Data show a remarkable scatter in the temperature region between 700K and 830K and the negative temperature coefficient behavior (NTC) looks much more accentuated in some sets of experiments.

It is interesting to observe that the most recent measurements suggest slower ignition delay times than older ones. Since reaction environment characterization plays such an important role, a heat exchange model has been implemented in our simulations. Two different approaches are generally adopted to account for the effect of heat loss. One is to include a heat loss term in the energy equation [10], and the other is to define a volume expansion term [11] so that heat loss is accounted for as a process of adiabatic expansion. This approach better represents a situation where the heat losses are limited to the region corresponding to the boundary layer, while the core of the reacting mixture is nearly adiabatic.
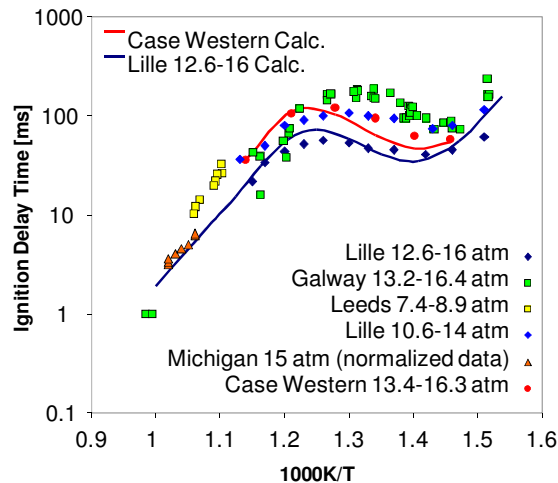

Fig. 1   Iso-octane experimental and calculated ignition delay times. Measurements have been carried out in different RCM facilities.

Then, a first set of experimental pressure profiles obtained out in non oxidative atmosphere has been used to calibrate the heat exchange model for the Lille RCM data. The reliability of the approach has been verified comparing model predictions with further non reactive experiments. The Case Western experiments have been simulated adopting the same approach, but assuming the heat loss parameters provided by the experimenters.

All the simulations have been carried out using the Chemkin package.

Figure 1 shows also two profiles of the calculated ignition delay time vs temperature. The agreement between experiments and calculation is generally satisfactory even if the model slightly underestimates the autoignition timing between 700K and 750K.

The faster ignition detected in the Lille RCM can be partially imputed to the lower heat exchange: still further investigations are necessary to identify the origin of the significant dispersion of data. This future study will also take advantage of the model capability of isolating the different sources of uncertainty.

3.2. 1-hexene comparisons

Differently from the primary reference fuels, a limited set of experimental information is available when large olefins are considered. Existing data refer mainly to those unsaturated hydrocarbon which better represent the olefins pertaining to gasoline blends. Several studies investigated the autoignition behavior of 1-pentene, 1-hexene and diisobutylene.

In this work we consider the 1-hexene data measured in the Lille RCM [12]. Since these measures were taken in the same device where the iso-octane ones were, the same heat loss model has been used. It should be remarked, though, that the lower ignition times characterizing this fuel are less affected by heat losses.

Figure 2 shows the comparison between experiments and calculations obtained at different pressures. The model shows a satisfactory agreement with the experiments: both the cool flame and the total ignition delay time are well reproduced.

The mechanism has been successfully validated also on shock tube and jet stirred reactor data in a wider range of operating conditions. Further details can be found in [5].
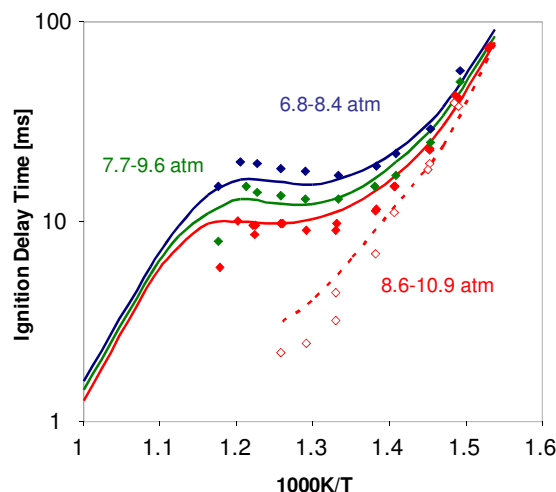

Fig. 2   1-hexene experimental and calculated ignition delay times. Calculations: solid line, experiments: symbols. Cool flames: dotted line corresponds to calculations, empty diamonds are experimental values

4. 1-hexene/iso-octane mixtures

A last set of comparisons involves the autoignition behavior of iso-octane/1-hexene mixtures. Once again the experimental data were taken at Lille facility [13]; therefore the same modeling approach is applied. The ignition delay times of an 82% iso-octane/18% 1-hexene mixture were measured in the 11.4-14 atm pressure range between 650K and 850K.

Figure 3 shows the experimental and calculated ignition times of the mixture as well as of the pure components at the same conditions. The model mimics well the autoignition behavior of the mixture. A non linear blending effect of 1-hexene on the autoignition properties is here well evident. Limited quantities of 1-hexene, >20%, decrease significantly the ignition delay

times of iso-octane. This can be easily explained considering the relatively large saturated portion of this alkene which allows some low temperature reactivity. The weak cool flame sustained by 1-hexene is in fact sufficient to start the low and intermediate temperature reactions of iso-octane.
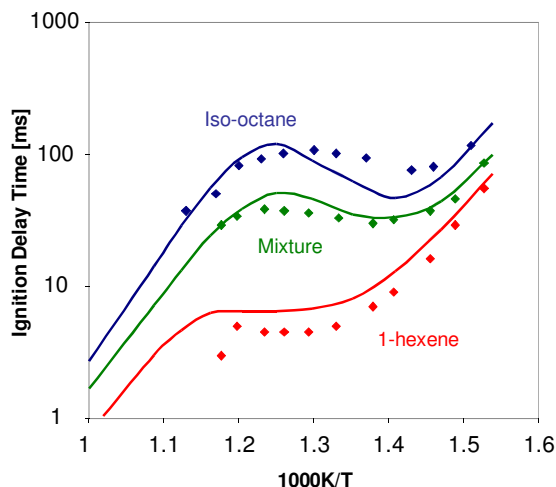

Fig. 3 Ignition delay times of an 88/12 iso-octane/1-hexene mixture at 11.4-14 atm. Pure components are reported as well. Experiments: diamonds, calculations: solid lines

The behavior of PRF mixtures and 1 hexene has been investigated by means of calculations. Figure 4 shows the pressure profiles of pure n-heptane, iso-octane and hexene calculated using the Lille RCM model and compares them with the ones obtained for two mixtures of the alkanes with the alkene. Both mixtures contain 50% alkane and 50% alkene. The temperature at the TDC is assumed to be 770K and the pressure 12.4 atm.

The reactivity of both the two mixtures is mostly influenced by the fastest fuel. The pressure and the temperature gains associated with the cool flame play a fundamental role in controlling the main heat release. At this temperature conditions the radical scavenging role played by the alkene is overridden by the low temperature chemistry of the saturated straight chains contained in the mixtures. The radical chain branching propensity of the fuel components is particularly important in the conditions here discussed, where the low temperature reactivity is nearly to extinguish resulting in the NTC region.

5. Conclusions

Some of the most relevant and recent improvements implemented in the NUI/LLNL kinetic mechanism have been described. The new versions of the iso-octane and n-heptane mechanisms were merged into a kinetic mechanism suited to gasoline surrogate kinetic modeling. Recent experimental information provided the basis for discussing some of the main issues related to gasoline like fuel experimental and modeling investigations, the mechanism has been used to simulate the ignition delay times of iso-octane, 1-hexene and their mixtures in a rapid compression machine. The model showed a good agreement with measured values.

The interactions between 1-hexene and PRF have been explained on the basis of calculations highlighting the role of the low temperature reactions in promoting the reactivity of the considered mixtures.

Further investigations involving both experiments and calculations will be aimed to identify a reliable set of experimental data and a good modeling basis for the validations of gasoline surrogate kinetic model.
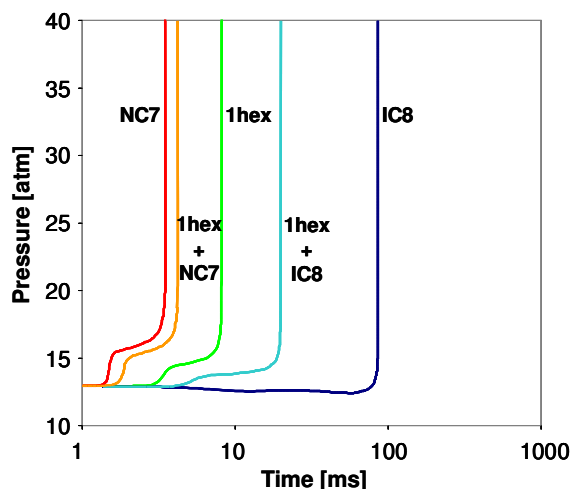

Fig. 4   Calculated pressure profiles of n-heptane (NC7), 1-hexene (1hex), iso-octane (IC8) and their mixtures.

6. Acknowledgments

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